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PENTA-COORDINATION OF ORGANOTIN COMPLEXES IN NON-AQUEOUS SOLVENTS

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It is known that organotin compounds have heen shown to possess coordination numbers higher than four. A recent review[1] reports a table of complex organotin compounds (adducts of $R_{4-n}SnX_n$ and donors such as ammonia, pyridine, etc.), the stoichiometry of which can be interpreted in terms of a coordination number preferentially of six. With regard to complex organotin hexa-coordinated anions[2], it has been pointed out that their stability falls as the number of electronegative halogen substituents decreases, giving the series:

$$SnCl_6^{2-} > RSnCl_5^{2-} > R_2SnCl_4^{2-} > R_3SnCl_3^{2-}.$$

Furthermore, the ability of triorganotin derivatives of the type R_3SnX to form autocomplexes containing a penta-coordinate Sn atom is well known[3]. Generally, compounds, where X is carboxylate, exist as linear polymers both in the solid state as well as in concentrated solutions[4]. The Me_3SnF structure shows association through fluorine atoms[5], and halogen bridging has also been suggested[6] for Me_3SnCl and Me_3SnBr. Penta-coordination in the solid state has been recognized for compounds in which X = perchlorate[7,8], fluoroborate[9,10], hexafluoroarsenate or antimonate[10], as well[7] as $[(CH_3)_3Sn(NH_3)_2]^+$ and[11,12] $(CH_3)_3SnCl(C_5H_5N)$. This last compound is the only example for which the structure has been determined: three methyl groups lying in an equatorial plane, with pyridine and chlorine axially oriented.

Complex organotin anions of the type R_3SnBrI^- and $R_3SnI_2^-$, (where R = methyl, ethyl, *n*-propyl and iso-propyl) are formed from trialkyltin halides with excess iodide in acetone[13]. These are the only examples of penta-coordinated organotin anions found in non-aqueous solvents.

It follows, then, that much work has been done on triorganotin derivatives, while little attention has been paid to the coordination compounds which can be formed in solution from substrates such as R_2SnX_2 and $RSnX_3$. Thus, we studied the complexes formed by chloride ion with the following series of compounds:

$PhSnCl_3$, Ph_2SnCl_2, Ph_3SnCl, and

$BuSnCl_3$, Bu_2SnCl_2, Bu_3SnCl,

in order to obtain information about the occurrence of penta-coordinated organotin anions in solution.

Potentiometric and conductometric titrations in acetonitrile and/or acetone were carried out. Tetraethylammonium chloride, trimethylammonium chloride and lithium chloride were used as chloride ion donors.

Potentiometric titrations

The acid—base system can consist of the conjugate couples

$$R_{4-n}SnCl_n/R_{4-n}SnCl_{n+1}^{1-} \quad \text{and/or} \quad R_{4-n}SnCl_{n+1}^{1-}/R_{4-n}SnCl_{n+2}^{2-}$$

(with $n = 1$, 2 or 3) in which chloride ion is the exchanged ligand.

Table I and II list the titration results in acetonitrile using tungsten or molybdenum electrodes, according to the method previously described[14,15].

TABLE I

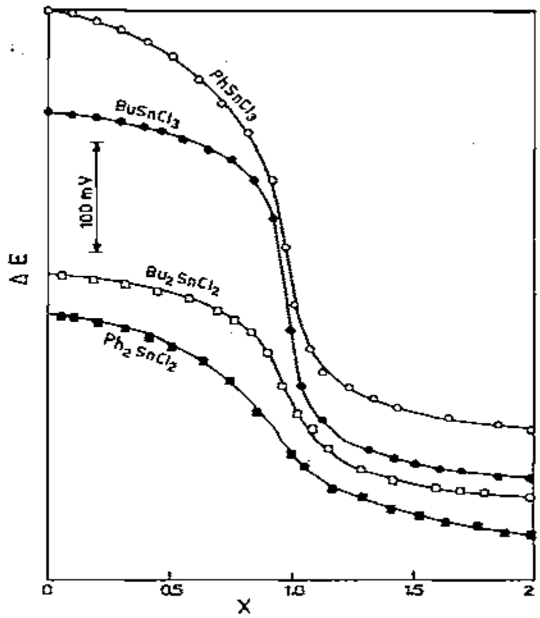
TITRATION OF Et_4NCl WITH $R_{4-n}SnCl_n$ COMPOUNDS ($n = 2$, 3) IN ACETONITRILE

Run No	*Concn. Et_4NCl (mole/l)*	*Titrated amount Et_4NCl (in ml)*	*Titrating compound*	*Concn. $R_{4-n}SnCl_n$ (mole/l)*	$X = \frac{R_{4-n}SnCl_n}{Et_4NCl}$, *at e.p.*
1	0.0120	25	$PhSnCl_3$	0.0618	0.995
2	0.0233	20	$PhSnCl_3$	0.0646	1.003
3	0.0233	10	$PhSnCl_3$	0.0646	0.998
4	0.0305	10	$BuSnCl_3$	0.0580	1.005
5	0.0177	18	$BuSnCl_3$	0.0580	1.000
6	0.0177	20	$BuSnCl_3$	0.0580	0.991
7	0.0305	15	Bu_2SnCl_2	0.0593	1.000
8	0.0200	20	Bu_2SnCl_2	0.0610	1.005
9	0.0250	15	Bu_2SnCl_2	0.0610	0.998
10	0.0690	6	Ph_2SnCl_2	0.1000	1.026
11	0.0345	15	Ph_2SnCl_2	0.1000	1.005
12	0.0345	20	Ph_2SnCl_2	0.1000	0.997

TABLE II

TITRATION OF $R_{4-n}SnCl_n$ COMPOUNDS ($n = 2$, 3) WITH Et_4NCl IN ACETONITRILE

Run No	*Titrated compound*	*Concn. $R_{4-n}SnCl_n$ (mole/l)*	*Titrated amount of $R_{4-n}SnCl_n$ (in ml)*	*Concn. Et_4NCl (mole/l)*	$\frac{1}{X} = \frac{Et_4NCl}{R_{4-n}SnCl_n}$, *at e.p.*
1	$PhSnCl_3$	0.0175	13.00	0.0305	0.993
2	$PhSnCl_3$	0.0640	1.85	0.0233	0.995
3	$PhSnCl_3$	0.0580	2.00	0.0120	1.005
4	$BuSnCl_3$	0.00228	26.00	0.0120	1.012
5	$BuSnCl_3$	0.0583	2.00	0.0177	1.015
6	$BuSnCl_3$	0.0510	1.00	0.0120	0.997
7	Bu_2SnCl_2	0.0593	3.50	0.0305	1.010
8	Ph_2SnCl_2	0.0685	3.00	0.0305	0.992



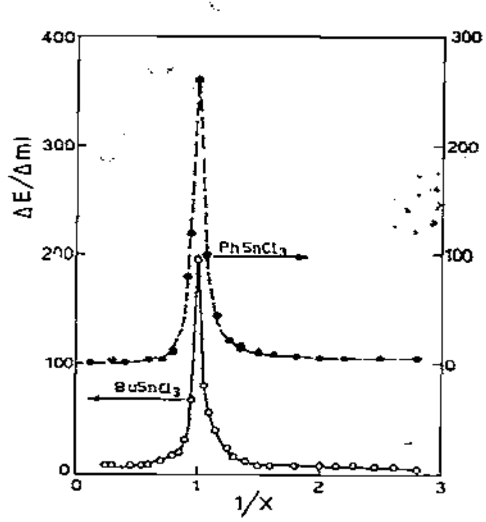


Fig. 1. Potentiometric titrations of Et_4NCl with $R_{4-n}SnCl_4$ compounds in acetonitrile. (Runs 1, 4, 7, 10 *cf.* Table I).

Fig. 2. Differential potentiometric plots of $R_{4-n}SnCl_n$ compounds with Et_4NCl in acetonitrile. (Runs 1, 4, *cf.* Table II).

Such titrations were possible only in the case of mono- and bi-organotin compounds. Figs. 1 and 2 show several examples of potentiometric plots: end points were found only for a 1:1 $R_{4-n}SnCl_n$:Et_4NCl ratio (X) indicating that the titration depends on the conjugate system:

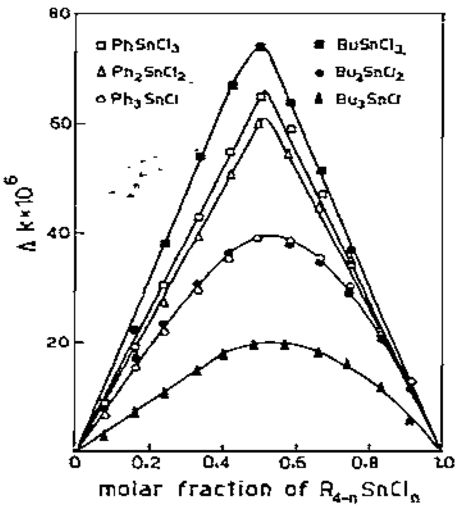
$$R_{4-n}SnCl_n/R_{4-n}SnCl_{n+1}^{1-},$$

where $n = 2$ or 3.

Conductometric titrations

Two series of runs were performed in acetonitrile and acetone by measuring the conductivity of mixed solutions of organotin compounds with trimethylammonium chloride and lithium chloride, respectively. Fig. 3 shows the continuous variation plots (specific conductivity *versus* molar fraction of organotin compounds) for all the described compounds. In this diagram Δk is the difference between the experimental value of k and the value calculated assuming no complex formation.

The continuous variation plots in acetone for equimolar mixtures of organotin compounds and lithium chloride are shown in Fig. 4: only those diagrams related to the mono-organotin derivatives are reported.



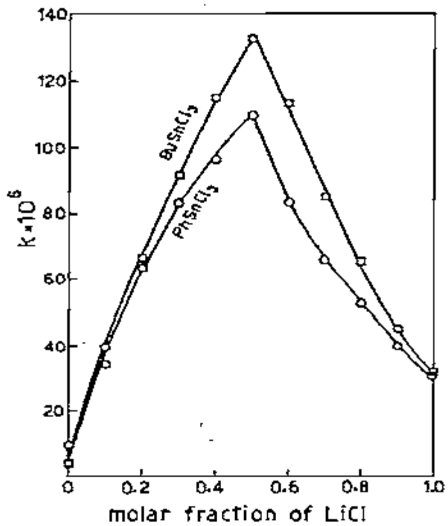


Fig. 3. Specific conductivity Δk of mixtures of equimolar solutions ($1.2 \cdot 10^{-3}$ mole/l) of $R_{4-n}SnCl_n$ compounds and Me_3NHCl against molar fraction of the organotin compound in acetonitrile.

Fig. 4. Observed specific conductivity k, of mixtures of equimolar solutions ($2 \cdot 10^{-3}$ mole/l) of $R_{4-n}SnCl_n$ and LiCl against molar fraction of lithium chloride in acetone.

In all Job's plots evidence was found for the formation of a 1:1 adduct between the examined metallorganic compounds and the complexing agent.

DISCUSSION

It is clearly evident that 1:1 adducts are generally formed in the case of triorganotin derivatives, indicating that a penta-coordinated structure is preferred over other alternative geometries based on four or six coordination. Penta-coordination for mono- and di-organotin would seem less likely: the expected model should be based on an octahedral configuration. In fact the majority of the observations made in literature[1] refer to 1:2 addition compounds with mono-dentate ligands and can be understood in terms of a coordination number of six.

From our experimental data it appears that, in solution, a penta-coordinated structure seems likely for all the examined compounds. It is worth remembering that potentiometric titrations of tetraethylammonium chloride with tin tetrachloride in acetyl chloride[14] show two equivalence points with molar ratio $X = 0.5$ and 1. The same results were obtained by means of conductometric measurements in the same solvent[16].

In addition our potentiometric measurements carried out in acetonitrile by titrating tetraethylammoniumchloride with tin tetrachloride indicate the formation in solution of the conjugate couples, $SnCl_6^{2-}/SnCl_5^-$ and $SnCl_5^-/SnCl_4$. Thus, tin tetrachloride behaves differently from the examined organotin compounds in such a solvent.

The occurrence of penta-coordinated complexes for the organotin compounds may be justified by a decrease in acceptor power upon substituting one chlorine atom by an organic group[17]. It seems that this is principally due to electronic effects instead of steric ones. Under comparable conditions chlorine is likely to be much more able than the organic groups to accomodate changes in its bonding to tin.

Since the butyl group is less electronegative than the phenyl group, the butyltin halo-complexes should be less stable than the phenyl analogs. From the obtained results, the following series:

$$PhSnCl_3 > BuSnCl_3 > Ph_2SnCl_2 > Ph_3SnCl > Bu_3SnCl,$$

indicates the complex forming ability.

In our opinion the fall from hexa- to penta-coordination for the examined complex ions in solution is just a general feature of organometallic chemistry: normally organohalogenosilanes[18], organomercury[19,20] and organolead[21] compounds in solution do not reach their maximum numher of coordination typical of the corresponding inorganic halides.

Nevertheless some examples, in which the maximum number of coordination is reached in metallorganic complex anions, have been reported: tetra-coordination has been ascertained for complexes formed by his(trifluoromethyl)mercury and trifluoromethylmercury iodide with halide ions[22], while $CH_3SnF_5^{2-}$ appears to have been detected in solution[23].

It seems to us that the occurrence of a detectable amount of the above species in aqueous solution depends on the highly electronegative groups attached to the metal atom. In these cases the ligands (CF_3, F) on the central atom are more able than the organic groups or the chlorine atom to assist in delocalization of the charge consequent to the formation of the coordinate bonds from tbese ligands.

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